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Published in:
Organic letters

DOI:
10.1021/ol060076l

Supporting Information

Phosphoric Acids as Amplifiers of Molecular Chirality in Liquid Crystalline Media

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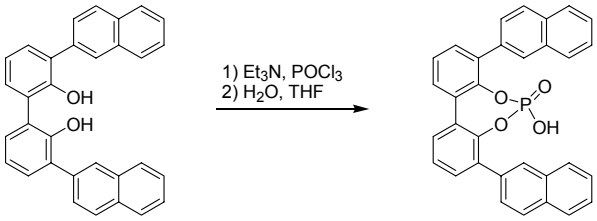
Synthesis

General remarks: Reagents were purchased from Aldrich, Acros Chimica, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. Reactions were performed using standard Schlenk techniques. Chromatography: silica gel, Merck type 9385 230-400 mesh, TLC: silica gel 60, Merck, 0.25 mm. Mass spectra (EI) were recorded on an AEI MS-902. Melting points were recorded on a Büchi B-545 melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury Plus, operating at 400 MHz for the ^{1}H nucleus, at 101 MHz for the ^{13}C nucleus, and at 162 MHz for the ^{31}P nucleus, in DMSO-d_6 or $CDCl_3$. Chemical shift values are denoted in δ values (ppm) relative to residual solvent peaks (DMSO-d_6, ^{1}H δ = 2.50, ^{13}C δ = 39.52; $CHCl_3$, ^{1}H δ = 7.26, ^{13}C δ = 77.00 ppm), or external H_3PO_4 (^{31}P, δ = 0.0 ppm). The synthesis of **2** was previously reported.[1]



S1 **1**

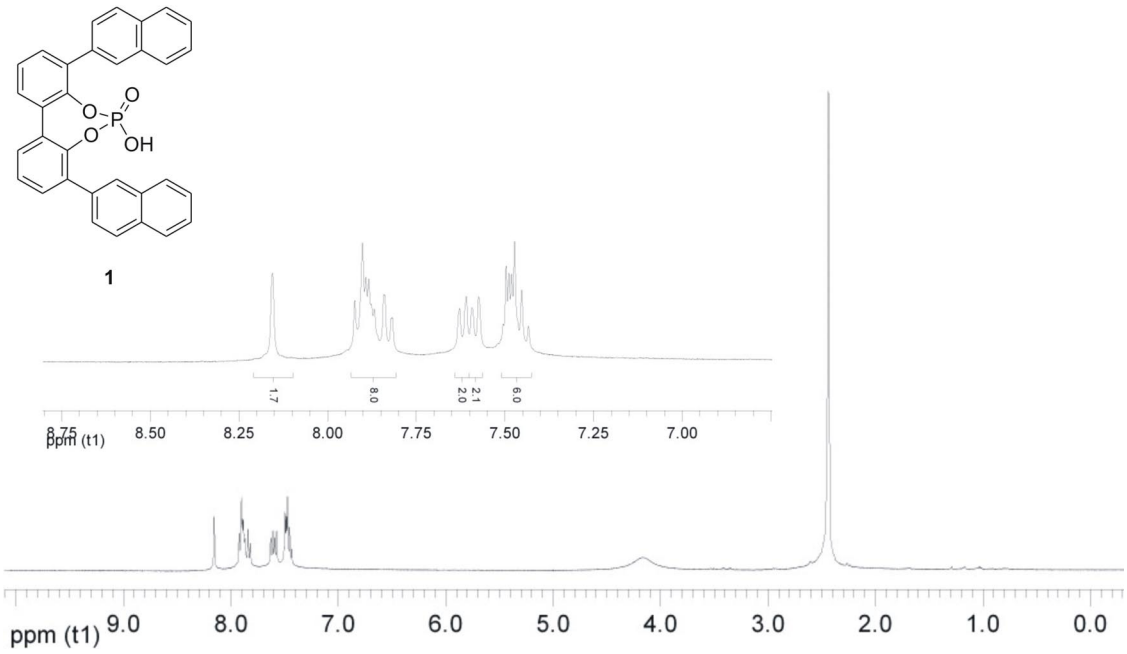
4,8-Di-naphthalen-2-yl-6-oxo-5,7-dioxa-6λ^5-phospha-dibenzo[a,c]cyclohepten-6-ol 1.

The synthesis of **S1** was previously described.[2]

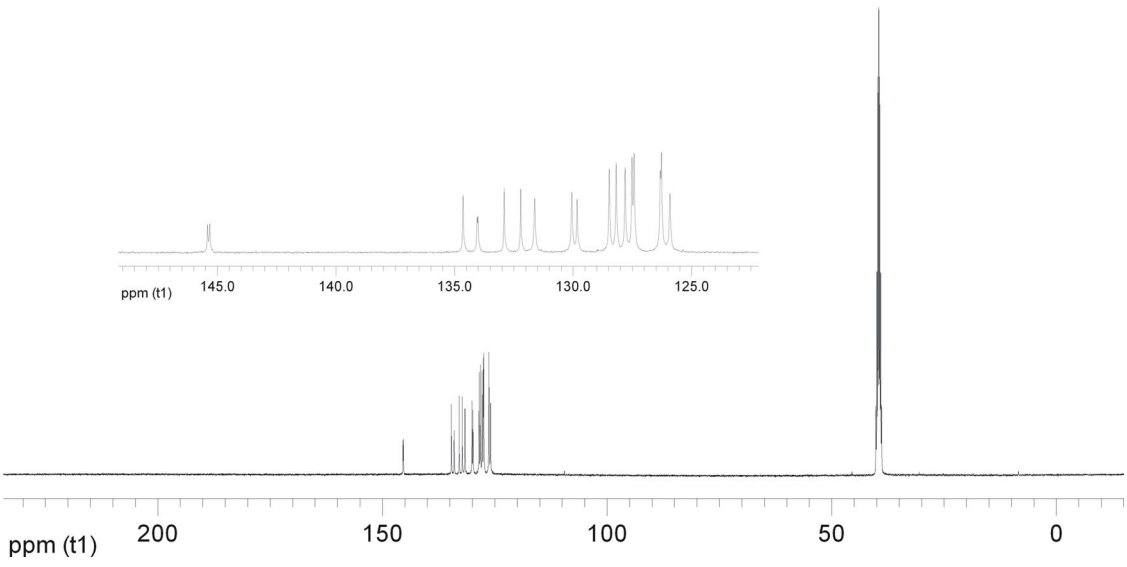
The synthesis of **1** was adapted from a literature procedure.[3]

Triethylamine (10.4 ml, 75.3 mmol) was added to a stirred solution of **S1** (1.1 g, 2.51 mmol) in dry CH_2Cl_2 (50 ml). $POCl_3$ (0.5 ml, 5.52 mmol) was added and the mixture was stirred for 3 h at 40°C. Subsequently the solvent was removed in vacuo, giving a yellow solid. This solid was suspended in a 1:1 mixture of THF and water (60 ml), which was then heated under reflux for 4 h. The resulting mixture was cooled to room temperature and the layers were separated. The aqueous layer was extracted twice with CH_2Cl_2. The combined organics were washed twice with water, dried over Na_2SO_4 and the solvent was removed in vacuo yielding a brown solid. Recrystallization from chloroform yielded **1** as a white solid (815 mg, 1.63 mmol, 65%). m.p. >330°C (dec.); ^{1}H NMR (DMSO-d_6) 8.23 (s, 2H), 7.93 (m, 8H), 7.67 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.54 (dd, J_1 = 3.3 Hz, J_2 = 6.2 Hz, 4H), 7.50 (dd, J_1 = 7.7 Hz, J_2 = 7.7 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) 145.4 (d, $J_{p\text{-}c}$ = 9.1 Hz), 134.6, 134.0 (d, $J_{p\text{-}c}$ = 3.7 Hz), 132.9, 132.2, 131.6, 130.1, 129.8, 128.5, 128.2, 127.8, 127.5, 127.4, 126.32, 126.27, 125.9; ^{31}P NMR (162 MHz) 0.46 (s); MS (EI): m/z 500 (M^+, 100%), 436 (M-PO_2H, 4%), 420 (M-PO_3H, 10%); Anal. Calcd. for $C_{32}H_{21}O_4P$: C, 76.79; H, 4.23; Found C, 76.85; H, 4.29; FT-IR (KBr, cm^{-1}) ν 3053, 2430, 2062, 1632, 1419, 1348, 1213, 1125, 1047, 966, 858, 820, 783, 741, 638, 579, 529, 479, 446. Phosphoric acid **1** is insoluble in $CDCl_3$. However, addition of 1 eq. of amine **3** or **4** led to a soluble complex, revealing small hydrocarbon peaks in the ^{1}H NMR spectrum at 1.26 and 0.85 ppm. This residue in the analytically pure sample could not be removed by repeated recrystallization or column chromatography, but was found not to interfere with the complex formation as no interactions were visible between this residue and **1** in the 2D NOESY spectrum of the complex of **1** with **4** (vide infra).

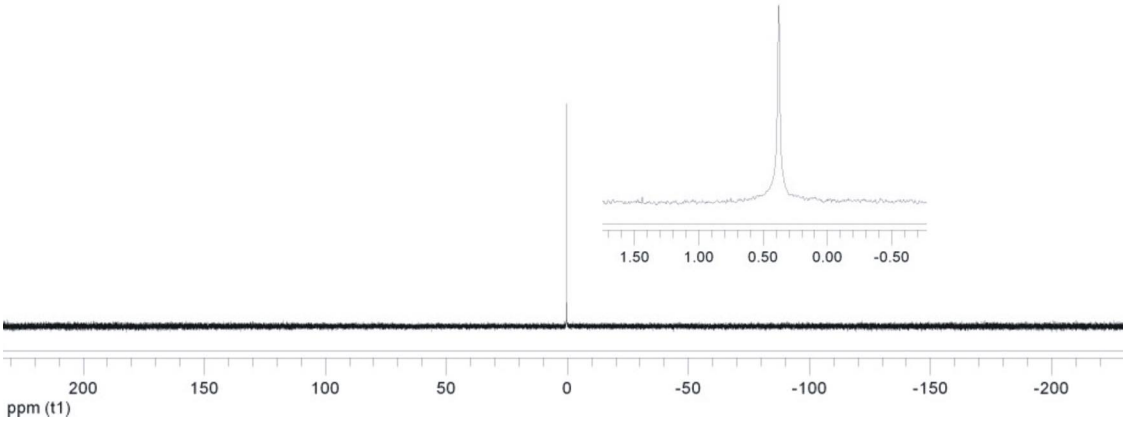
^{1}H NMR (DMSO-d_6) of **1**



^{13}C NMR (DMSO-d_6) of **1**



^{31}P NMR (DMSO-d_6) of **1**



Measurements

General remarks: all solvents were HPLC or spectroscopic grade, and were used as received. The liquid crystalline material E7 was purchased from Merck, Darmstadt. Commercially available amines **3**-**10** were dissolved in methanol and the solution was filtered over a plug of SiO_2. After evaporation of the solvent, they were stored under N_2.

General procedure for determination of the cholesteric pitch

The pitch of the liquid crystalline (LC) phases was determined by Grandjean-Cano technique,[4] using plane-convex lenses of known radii (R = 25.119 or 30.287 mm, Linos Components; Radiometer), and an Olympus BX 60 microscope equipped with a Linkam THMS 600 hotstage. LC phases were aligned on a glass surface (typically 6.25 cm^2) that was spin-coated with commercially available polyimide AL1051 (purchased from JSR, Belgium) and linearly rubbed with a velvet cloth. Using stock solutions of amines and **1** in THF, mixtures of these two compounds were made. The THF was removed under reduced pressure, and E7 (stock solution in toluene) was added. This solution was applied on a linearly rubbed, polyimide-coated glass plate and after the toluene had evaporated in the air, the glass plate was placed under the microscope. After applying a plane-convex lens of known diameter, Grandjean-Cano lines could

be observed in the described cases, and the pitch could be determined by measuring the distances between the consecutive lines. When, as a control experiment, mixtures of E7 with only receptor **1** or only amines **3**-**11** were made, no cholesteric textures or Grandjean-Cano lines were observed. The sign of the helical pitch was determined with a contact method,[5] where mixing of the samples with a doped cholesteric liquid crystal of known negative screw sense, consisting of dopant ZLI-811 (Merck, Darmstadt, Germany) in E7, was tested. To check if the difference in pitch as described in Table 1 was not a result of a difference in clearing temperature between the complexes, the clearing temperatures of mixtures of E7 with complexes **1•3**, **1•4**, **1•5** and **1•11** where determined. In all four cases the same clearing temperature was observed (T_c = 58.4 ± 0.3 °C). As the clearing temperature of E7 with only amines **3**, **4** or **5** (T_c = 59.2 ± 0.2 °C), is higher than for the complexes the lack of cholesteric induction by the sole amines can not be ascribed to a depression in clearing temperature. To assess the influence of the receptor/amine ratio on the cholesteric pitch, 6 samples of different ratio were prepared and their pitch was measured. The concentration of **1** was kept constant at 0.038 μmol/mg E7. Figure S1 shows the pitch change vs. the equivalents of amine **3** added.

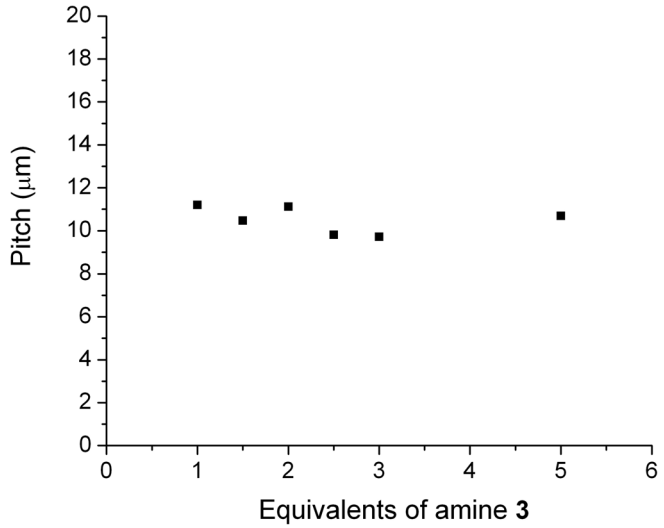


Figure S1. Cholesteric pitch vs. equivalents of amine **3**.

^{1}H NMR titration

The 1:1 binding stoichiometry of the **1•3** complex was confirmed as follows. Receptor **1** is insoluble in $CDCl_3$, but when amine **3** is added, **1** is dissolved through complexation. Therefore, an NMR tube was filled with 4.8 mg **1**, 0.5 ml $CDCl_3$ and 5 μl acetone as internal standard, generating a suspension. No ^{1}H NMR signals for **1** were observed. Upon addition of 0.25 eq. portions of a stock solution of **3** (5.05 mg in 0.4 ml $CDCl_3$), the complex went into solution, resulting in an NMR signal for **1** and **3**. By integration of the signals associated with **1** and comparing them to the acetone signal, the amount of dissolved complex could be estimated. When the relative signal of **1** compared to acetone was plotted against the number of equivalents of **3** added, a gradual increase up to 1 eq. was observed (Figure S2). Addition of more equivalents of **3** resulted in almost no change in the amount of **1** in solution, indication 1:1 complexation. This conclusion is supported by the visual observation that it takes 1 eq. of **3** to make **1** dissolve in $CDCl_3$.

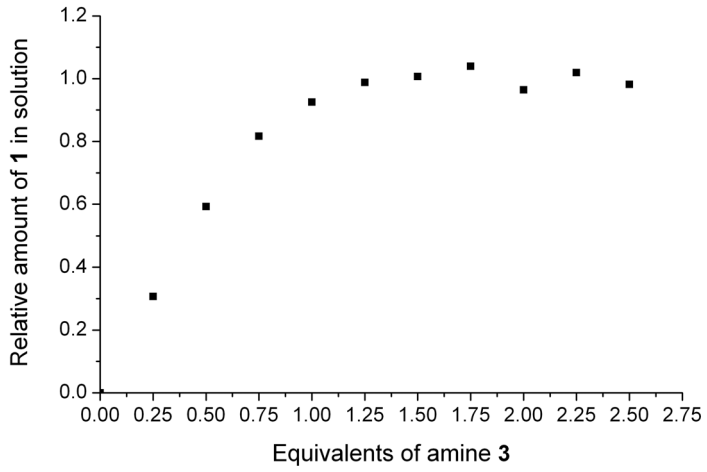


Figure S2. Amount of receptor **1** in solution in response to addition of amine **3**.

^{1}H NMR of complexes 2•3 and 1•3.

Mixing of **1** and **3** leads to an upfield shift of both aromatic (H_X, H_Y, H_Z) and aliphatic (H_U, H_V) protons of **3**. When **3** is mixed with **2**, this effect is much less pronounced, indicating that it is caused by the shielding of the protons of **3** by the naphthalene moieties on **1** (Figure S3).

Conditions: **1•3**, [**1**] = [**3**] = 0.04 M in $CDCl_3$; **2•3**, [**2**] = [**3**] = 0.04 M in $CDCl_3$; ambient temperature, 400 MHz.

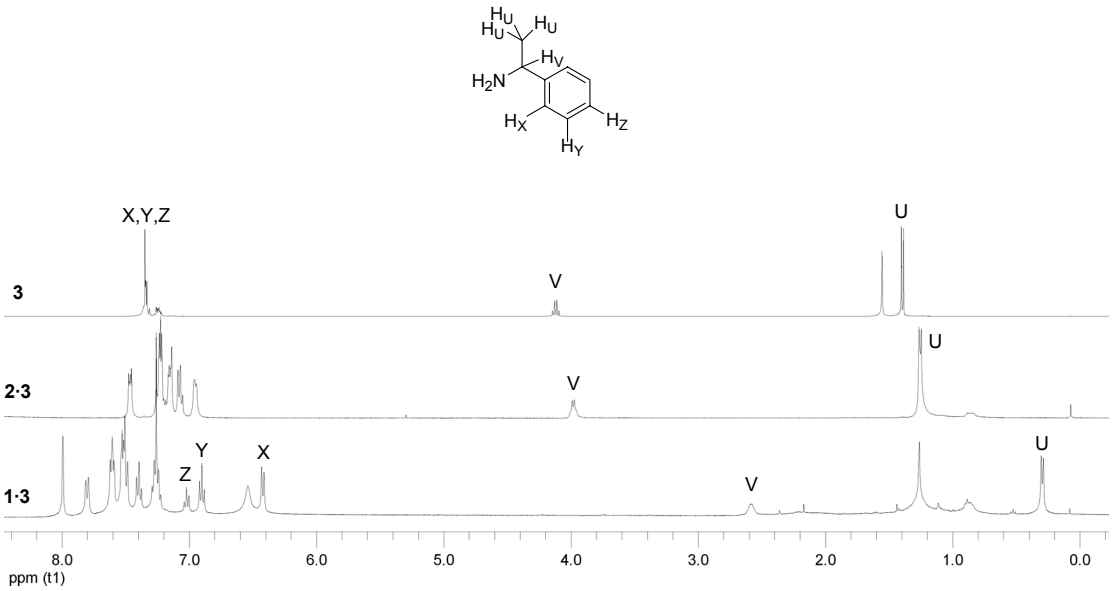


Figure S3. ^{1}H NMR of **3**, **2•3** and **1•3** in $CDCl_3$.

2D NOESY of 1•4.

The 2D NOESY spectrum of **1•4** was recorded at 500 MHz on a Varian Unity Plus Varian-500, using a mixture of **1** (0.045 M) and **4** (0.045 M) in $CDCl_3$. The mixing time was set to 0.7 s. In the areas marked by the dotted lines the interactions between the naphthalene protons of **1** and some aromatic and aliphatic protons of **4** are visible.

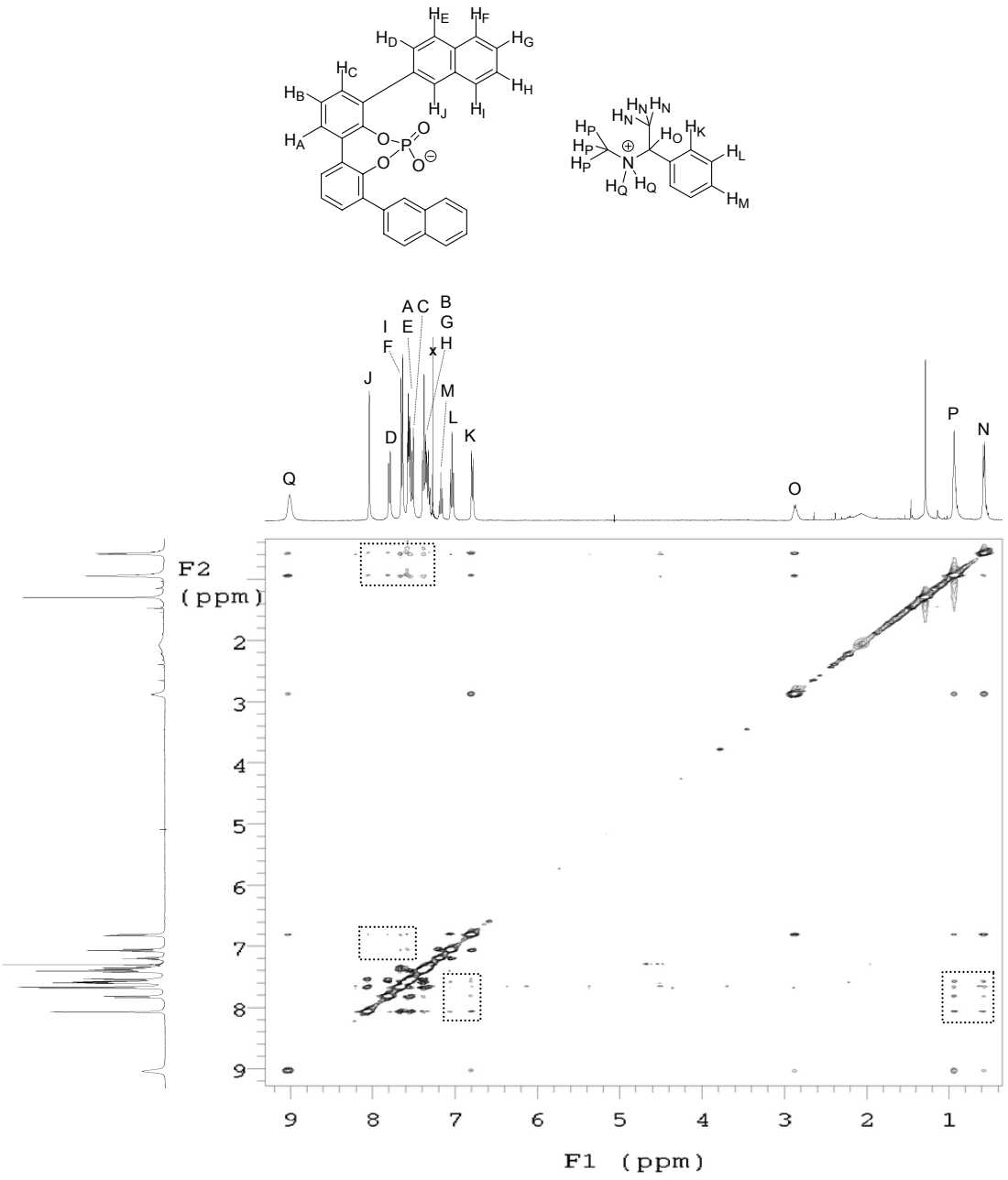


Figure S4. 2D NOESY spectrum of **1•4**.

Circular dichroism measurements

CD spectra were recorded on a JASCO J-715 spectropolarimeter and UV measurements were performed on a Hewlett-Packard HP 8453 FT spectrophotometer using UVASOL grade $CHCl_3$ (Merck) in a 1.0-mm quartz cell at ambient temperature (20-25ºC). For all, [**1**] = $4.04*10^{-4}$ M, [amine] = $4.04*10^{-2}$ M (100 eq.).

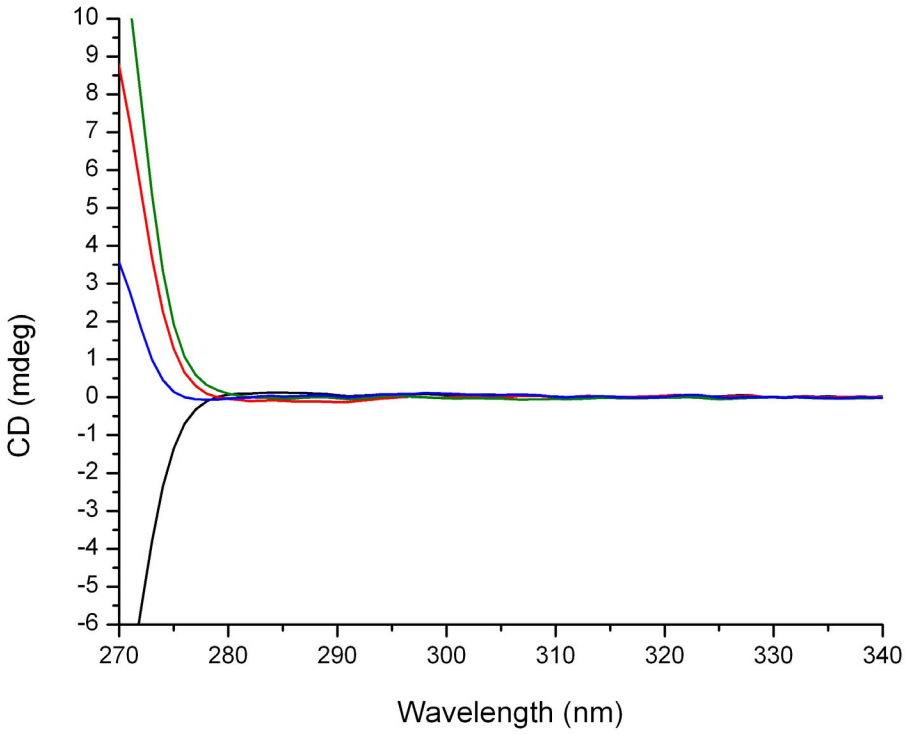


Figure S5. CD spectra of amines **3**, **4** and **5** without added receptor **1**. [amine] = $4.04*10^{-2}$ M. (*S*)-**3** (red line), (*R*)-**3** (black line), (*S*)-**4** (green line), (*S*)-**5** (blue line).

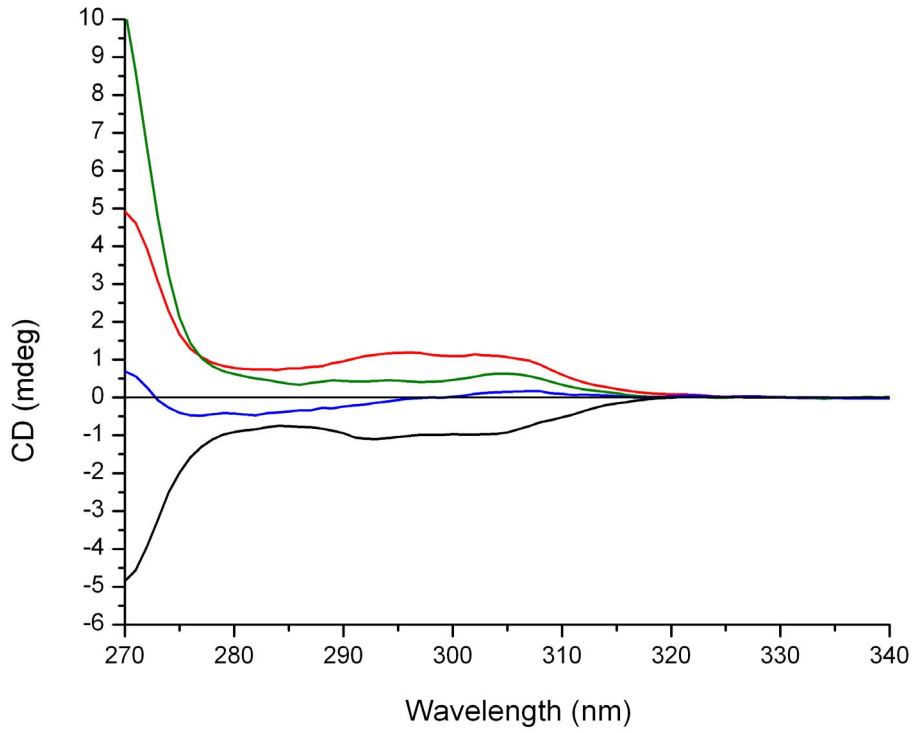


Figure S6. CD spectra of complexes **1•3**, **1•4** and **1•5**. **1**•(*S*)-**3** (red line), **1**•(*R*)-**3** (black line), **1**•(*S*)-**4** (green line), **1**•(*S*)-**5** (blue line).

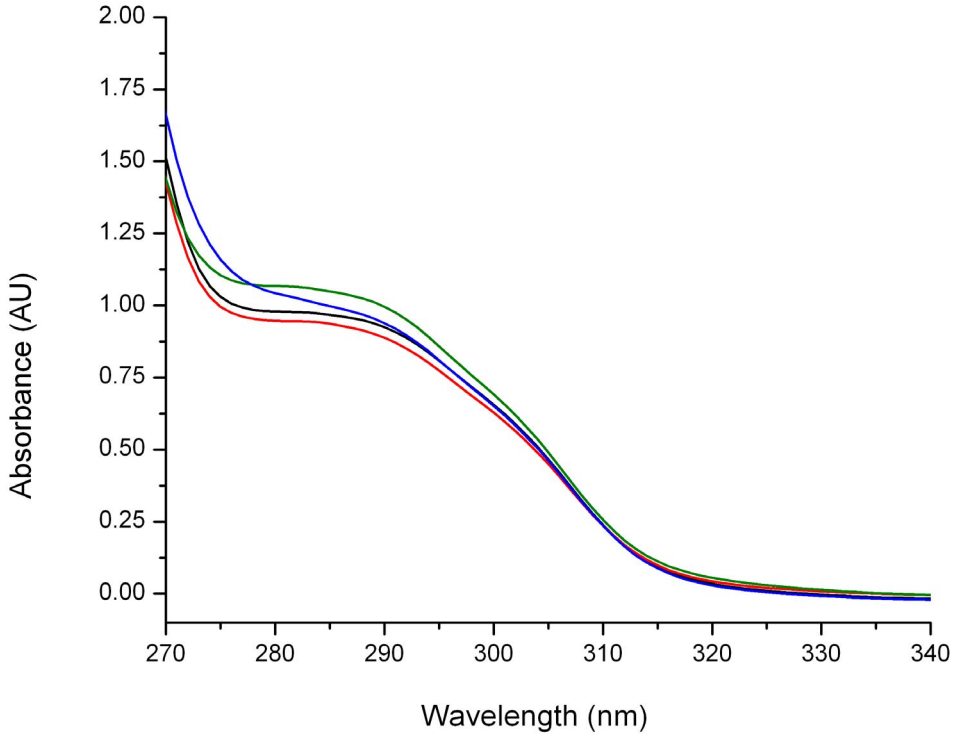


Figure S7. UV spectra of complexes **1•3**, **1•4** and **1•5**. **1**•(*S*)-**3** (red line), **1**•(*R*)-**3** (black line), **1**•(*S*)-**4** (green line), **1**•(*S*)-**5** (blue line).

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